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**SURFACTANT REMOVAL STUDY FOR NANO-SCALE
SmCo₅ POWDER PREPARED BY HIGH ENERGY BALL
MILLING (POSTPRINT)**

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Surfactant Removal Study for Nano-Scale SmCo₅ Powder Prepared by High Energy Ball Milling

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In the present study, nano-flake SmCo₅ powders with typical flake thickness of 300 nm were prepared by high energy ball milling using valeric acid as a surfactant. In order to remove the surfactant the as-milled powders were heat treated in argon and the effect of the annealing temperature on structural and magnetic properties of the resulting SmCo₅ powder was investigated. Partial (58%) and nearly complete (96%) surfactant removal was observed by DSC after treatments at 200 °C and 400 °C, respectively, without oxide formation detectable by powder X-ray diffraction. Demagnetization measurements revealed suppression of the energy product (BH)_{max} and dramatic decrease in coercivity (H_{ci}) after annealing. The results indicate that even a modest heat treatment of SmCo₅ nano-powder severely degrades its magnetic properties. Either alternative methods of surfactant removal must be considered, or the surfactant must remain during further powder processing.

Index Terms—High energy ball milling, magnetic properties, surfactant removal, SmCo₅.

I. INTRODUCTION

SURFACTANT-ASSISTED high energy ball milling (HEBM) has become a viable tool for production of various micro- and nano-scale powders used in a wide range of materials science applications. For magnetic alloys, HEBM is employed as a method for preparation of nano-scale anisotropic rare-earth magnetic powders with controlled particle size and morphology [1]–[7]. Final powder particle properties depend on the milling process parameters such as milling time, ball-to-powder mass ratio, and, most critically, choice and the relative amount of the surfactant [8]–[10]. During the milling process surfactant molecules adhere to the freshly exposed particle surface creating a thin organic layer. This layer protects the particles from mechanical alloying when they come in contact with each other further in the milling process. Organic fatty acids are typically used as surfactants; their molecules contain carboxylic functional components which form carboxylate bonds with the metal surface and long molecular chains which create an electrostatic barrier for the surrounding powder particles. Recently, surfactant-assisted HEBM has been used in preparation of nanostructured SmCo₅ magnetic powders with anisotropic flake-like morphology and particle thickness below 100 nm [4], [6], [11], [12].

Surfactants play an essential role in HEBM process, however, they often need to be removed after milling and prior to a powder consolidation step. The presence of surfactant during powder sintering or hot pressing may result in organic material decomposition or reaction with the base metal alloy producing impurities in the final product. Typically surfactant re-

moval is achieved through a vacuum annealing process which requires relatively high temperatures and long dwelling times. Such thermal conditions are undesirable for treatment of nanostructured powders, since exposure to elevated temperatures results in grain growth and oxidation [9], [13]. A recent study has shown that heat treatment temperature depends on surfactant molecular weight (MW) and it can be reduced by using surfactants with shorter molecular chains. Oleic acid (OA) is the most commonly used surfactant reported in the literature for preparation of SmCo₅ nano-flake powders [6], [7], [9], [12]. Due to its chemical interaction with the metal, temperatures above 500 °C under atmospheric conditions are required for OA removal (OA boiling point is 360 °C, MW = 282 g/mol). A lower molecular weight surfactant such as valeric acid (VA, boiling point 185 °C, MW = 102 g/mol) would require a less aggressive heat treatment and may be more suitable for SmCo₅ alloy powder processing [10].

In the present work SmCo₅ nano-flake magnetic powder were prepared by HEBM using valeric acid. Different annealing conditions for surfactant removal were investigated. The effect of the heat treatment has been evaluated by estimation of residual surfactant content and magnetic property comparison between the as-milled and treated SmCo₅.

II. EXPERIMENTAL

Pure Sm and pure Co were combined in a 1:5 atomic ratio and are melted into a SmCo₅ alloy button in Ar atmosphere. The button was mechanically crushed into coarse powder (particle size under 250 μm) which was used as the starting material for high energy ball milling. For HEBM the SmCo₅ powder (5 g), milling balls (1/8" diameter, hardened stainless steel, 20 g, 152 balls), vehicle (heptane, 2.75 g, Acros Organics) and surfactant (valeric acid, 1.5 g, Aldrich) were combined and sealed under Ar atmosphere in a stainless steel jar and milled in a SPEX 8000D vibratory mill for 1 h. After milling the powders were rinsed with acetone, vacuum dried, and separated from the ball media.

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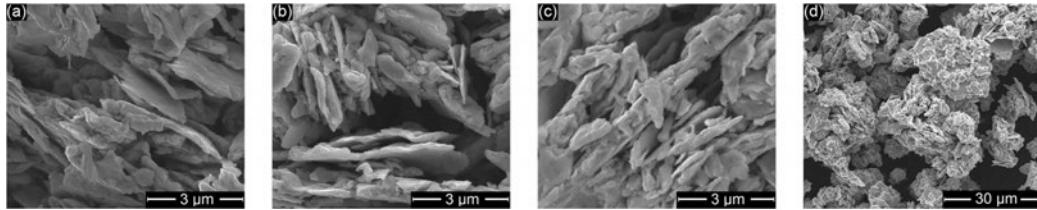


Fig. 1. SEM images of as-milled (a), heat treated in argon at 200 °C (b) and 400 °C (c) SmCo₅ nano-flake powders prepared by HEBM using valeric acid; clusters of SmCo₅ nano-flakes (d).

The as-milled SmCo₅ powders were heat treated at two different temperatures: 200 °C and 400 °C. In order to avoid oxidation an argon atmosphere was used at a pressure slightly above atmospheric (800 torr); treatment in air was also conducted (at pressure ~1 torr) for comparison. Relative contents of residual surfactant were compared by DSC analysis, Perkin Elmer DSC 8000, temperature range 30 °C to 600 °C, heat rate 20°/min, in flowing high-purity Ar. The presence of metal oxides and primary SmCo₅ phase were evaluated by X-ray diffraction (XRD) data collected on beamline 33-BM-C [14] at the Advanced Photon Source of Argonne National Laboratory, using X-ray radiation with wavelength $\lambda = 0.0589605$ nm. Measurements were performed on powder samples mounted in quartz capillaries and using a curved image plate detector in the 2θ angular range 3.5°–35.5°; additional procedure details are described in [15]. Powder morphology before and after heat treatment was investigated with SEM, FEI Quanta ESEM. For magnetic property measurements SmCo₅ powders were combined with an epoxy resin (80% powder, 20% epoxy by mass), pulse magnetized in a 10 T magnetic field, and set for curing between permanent magnets in a field ~1 T for 24 h. A KJS Associates closed-loop hysteresisgraph (model MG-700) was used to measure magnetic behavior of the cured samples and determine magnetic coercivity H_{ci}, remanence B_r, and maximum energy product (BH)_{max}.

III. RESULTS AND DISCUSSION

SEM imaging of the as-milled and heat treated SmCo₅ powders prepared by HEBM using valeric acid (Fig. 1) revealed a highly anisotropic flake-like morphology with flake sizes in the range 1–5 μm wide and 200–600 nm thick. Formation of flake-shaped particles is consistent with previous experiments [4]–[7] and is facilitated by the presence of the surfactant during HEBM. A preliminary study has also been conducted to determine effect of milling time on the SmCo₅ nano-flake thickness. The selected time of 1 h produced 200–600 nm flakes which according to [7] results in relatively high energy product (BH)_{max}. The flake dimensions are also in agreement with previous reports using oleic acid as a surfactant. However, no study of relation between milling parameters and final powder morphology for the case of valeric acid has been done.

Comparison between SEM images of the untreated powders and treated at 200 °C and 400 °C (both in Ar and Air atmospheres) did not show any visible differences in the powder morphology, even though an onset of particle coagulation was expected after the heat treatment. Presence of the organic surfactant in the as-milled powder was indirectly evidenced by minor

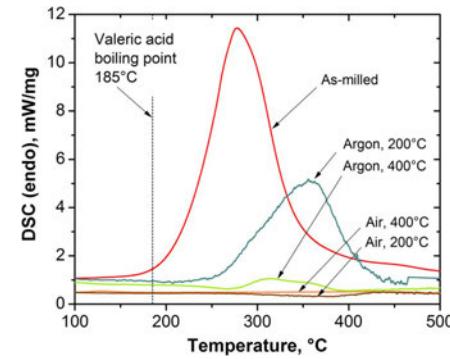


Fig. 2. DSC heat flow (heating) for as-milled and heat treated SmCo₅ nano-powders.

charging during SEM raster due to lower powder surface conductivity. TEM imaging would be more suitable for a detailed particle surface analysis and estimation of the surfactant layer thickness.

Residual surfactant content was estimated from DSC analysis with the data shown in Fig. 2. For the as-milled powder a large endothermic peak with an onset near the valeric acid boiling temperature (185 °C) indicated the presence of the surfactant. Powders heat treated in Ar exhibit similar peaks but with the peak area decreasing for higher dwell temperatures, which is evidence of a reduced amount of the surfactant. In addition, the peak onset temperature shifts toward higher values suggesting stronger bonding of the valeric acid to the metal particles as the surfactant layer becomes thinner. Detailed peak area comparison showed partial (58%) and nearly complete (96%) surfactant removal after treatment in Ar at 200 °C and 400 °C, respectively. Treatment in air at reduced pressure resulted in full surfactant removal; no DSC peak from valeric acid was observed after either dwell temperatures. This can be attributed to the reduced boiling point of the surfactant due to lower air pressure (1 torr) than Ar (800 torr) during annealing. Also the presence of oxygen facilitates organic surfactant decomposition in addition to evaporation.

Exposing SmCo₅ powder to air at elevated temperatures resulted in oxidation as indicated by CoO, Co₃O₄, and Sm₂O₃ oxide XRD peaks (Fig. 3). The oxide peaks progressively become sharper and more pronounced corresponding to larger metal oxide volume fraction and crystallite size formed after annealing at higher temperature. Note that the initial SmCo₅ phase was not detected among the metal oxides, which is discussed later in the text. On the other hand, no oxide formation was observed after treatment in Ar, which confirms that excess

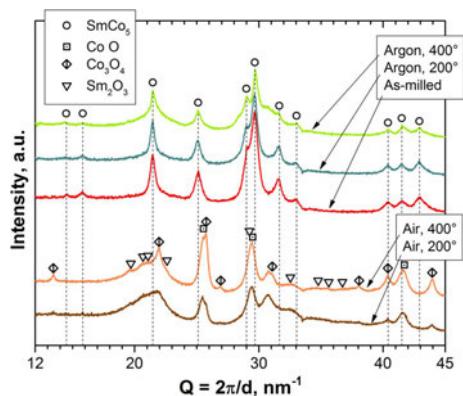


Fig. 3. Powder XRD data for as-milled and heat treated SmCo₅ nano-scale powder.

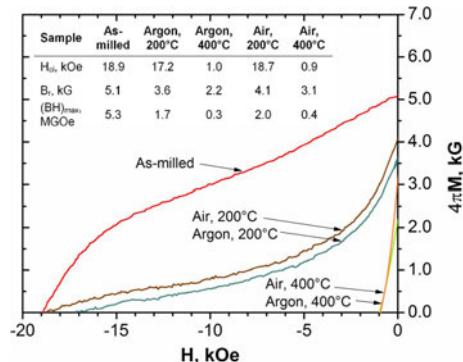


Fig. 4. Demagnetization data for epoxy bound as-milled and heat treated SmCo₅ nano-powders. Inset table: coercivity H_{ci}, remanence B_r and maximum energy product (BH)_{max}.

Ar pressure is highly effective in preventing oxygen access to the powder and avoiding alloy oxidation.

Demagnetization data for all heat treated and as-milled SmCo₅ powders are shown in Fig. 4. The heat treatment at 200 °C results in significant reduction of the maximum energy product (BH)_{max} to 1.7 MGOe down from 5.3 MGOe (see Fig. 4 inset table), which is further degraded after treatment at 400 °C to 0.3 MGOe. Strong suppression of the M(H) curve squareness and appearance of a slope change around H ~ 3 kOe after annealing at 200 °C suggests gradual development of a SmCo₅ volume fraction with much lower coercivity H_{ci} than the initial untreated SmCo₅. This fraction is further expanded to the full SmCo₅ volume after 400 °C treatment leading to overall deterioration of H_{ci} and (BH)_{max}. As shown in previous reports the coercivity of SmCo₅ nano-flake powders strongly depends on the particle thickness [7], [16] reaching its maximum of 20 kOe for 180 nm flakes. In the present study the average thickness of SmCo₅ flakes is around 300 nm and measured coercivity for the untreated samples H_{ci} = 18 kOe agrees well with the above reference. Particle growth would be the first choice to explain the decrease in magnetic coercivity, however, according to SEM no significant particle sintering or merging were observed. Moreover, even micron thick flakes produced by HEBM still exhibit H_{ci} around 10 kOe [16], while a decrease in H_{ci} by a factor of 15–20 is observed after the heat treatment in the present 300 nm powder. Therefore, it was

assumed that the coercivity mechanism is strongly related to the specifics of the ball milling process and structural dynamics within individual particles during annealing.

There are several factors affecting the coercivity in SmCo₅ powders. Magnetization reversal process is strongly related to the magnetic domain nucleation and domain wall motion. In a defect-free single domain particle magnetization reversal would require cooperative rotation of all magnetic spin moments producing the highest coercivity due to strong magnetocrystalline anisotropy of SmCo₅ [17]. However, the coercivity decreases dramatically with the presence of domain nucleation sites such as structural defects, chemical impurities, surface edges, etc., most of which concentrate close to the particle surface. On the other hand, similar defects within the bulk of the particles serve as domain wall pinning centers inhibiting domain wall propagation through the particle thus enhancing its coercivity [18]–[20]. As a result of the ball milling process large amounts of both surface and bulk defects are produced in SmCo₅ powder giving the resultant H_{ci} values.

It has been shown in literature that lower coercivities in SmCo₅ powders were observed with aging or annealing due to decrease in concentration of bulk domain wall pinning centers [18]. Additionally, surfactant reacting with SmCo₅ at elevated temperatures creates chemical uniformities on particle surfaces thus increasing domain nucleation site concentration and further degrading the coercivity. It is believed both above mechanisms contribute to the strong suppression of (BH)_{max} in the present heat treated SmCo₅ nano-powders.

An attempt was made to estimate SmCo₅ average grain size from the XRD peak geometry using Scherrer's equation [21]

$$\text{Size} = \frac{k \cdot \lambda}{\cos(\theta) * (\text{FWHM})}$$

where λ is the X-ray wavelength, k is a shape factor, 2θ is the peak center position, and FWHM is peak width. Gaussian and Lorentzian equations were used to fit several peaks and the average grain size was calculated as 10.3 ± 1.7 nm, 11.2 ± 1.5 nm, and 9.5 ± 3.4 nm for untreated, treated at 200 °C and 400 °C powders, respectively. These results do not show a trend in grain growth.

Interestingly enough, the difference between magnetic response, namely in (BH)_{max} energy product, for SmCo₅ samples treated in Ar and air is relatively small (around 20%) compared to the effect of the annealing temperature (by a factor of 3–4) despite heavy oxidation in air-treated SmCo₅ (Fig. 3). Taking into account that slight variation in measured remanence B_r and coercivity H_{ci} between samples is expected due to some inconsistency in sample preparation steps we assumed M(H) data (Fig. 4) for air and Ar-treated SmCo₅ are approximately the same with no significant atmosphere effect.

Such a result indicates a contradiction: the SmCo₅ phase was not observed in the air-treated powder, but its magnetic response is very close to the unoxidized SmCo₅ annealed in Ar at the corresponding temperature. Initially we assumed only an insignificant fraction of SmCo₅ transformed into an oxide forming a thin layer on particle surfaces without affecting magnetic response but masking the underlying nonoxidized phase from detection by XRD. The X-ray attenuation length in SmCo₅ is

under $10\ \mu\text{m}$ for the beamline photon energy (21 keV) and incidence angles ($2\theta = 3.5 - 25^\circ$) used in this study [22] and the information depth is on the order of several microns. This depth is much larger than average powder flake thickness ($\sim 300\ \text{nm}$) and is comparable with the flake lateral dimensions ($1 - 5\ \mu\text{m}$). In this case absence of the initial SmCo_5 phase peaks would imply complete particle oxidation without a remaining SmCo_5 core, which contradicts the magnetic response data. Alternatively it is suggested that flake agglomeration into clusters [Fig. 1(d)] due to magnetostatic interaction results in a large amount of the SmCo_5 protected from exposure to oxygen at the cost of oxidation of a few outer cluster flake layers. For the observed cluster size of $5 - 30\ \mu\text{m}$ this assumption qualitatively agrees with the XRD and demagnetization results, however, additional investigations such as neutron diffraction and TEM are needed for better understanding of the metal oxide presence in the heat treated SmCo_5 powders.

IV. CONCLUSION

Nano-flake SmCo_5 powders were prepared by surfactant-assisted high energy ball milling using a low molecular weight valeric acid surfactant. Final powder morphology showed flake shape and dimensions (width $1 - 5\ \mu\text{m}$ and thickness $200 - 600\ \text{nm}$) similar to previously prepared powders using conventional oleic acid. A heat treatment approach for the surfactant removal was investigated. Annealing at $200\ ^\circ\text{C}$ and $400\ ^\circ\text{C}$ in argon resulted in partial (58%) and nearly complete (96%) valeric acid removal and avoided powder oxidation. However, the magnetic energy product (BH_{max}) strongly degraded from 5.3 (as-milled) to 1.7 ($200\ ^\circ\text{C}$) and 0.3 MGoe ($400\ ^\circ\text{C}$) after the heat treatment, which was attributed to suppressed coercivity due to generation of domain nucleation sites (surface defects) and reduced concentration of domain wall pinning centers (bulk defects) within individual flakes. Annealing in air has led to complete surfactant removal but also thin surface oxide layer formation, which did not significantly affect the magnetic properties.

In summary, the results of the present study indicate that even a modest heat treatment of SmCo_5 nano-powder prepared by HEBM severely degrades its magnetic properties regardless of the atmosphere. The heat treatment process is not suitable for surfactant removal and either alternative methods must be considered, or the surfactant must remain during further powder processing.

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